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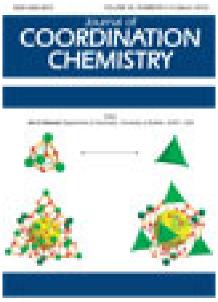

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Synthesis, characterization, and density functional study of some manganese(III) Schiff-base complexes

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Some Mn(III) complexes of *N*,*N′*-(2-hydroxy)propylenebis(acetylacetoneimine) (abbreviated to H_2L^1) and *N*,*N′*-(2-hydroxy)propylenebis(2-imino-3-oximino)butane (abbreviated to H_2L^2), [Mn(III)(Lig)(X)] (where Lig stands for the dianion of the Schiff-base ligands and X stands for CH_3COO^-, Cl^-, Br^-, I^-) were synthesized. The complexes are characterized with the help of elemental analyses, magnetic moments, spectroscopic data (UV-Vis, infrared), and molecular weight determination (measured by Rast's method). The structures of the complexes were obtained using density functional theory (DFT). DFT calculation shows that **1**–**4** and **8** are trigonal-bipyramidal whereas **5**–**7** are square-pyramidal.

Keywords: Manganese(III) complexes; Density functional study; Vibrational spectra; Trigonal-bipyramidal geometry

1. Introduction

Interest in coordination chemistry of manganese is gaining importance due to its involvement in a number of biological systems [1–4], especially in its high oxidation states. Kochi, Jacobsen, and Katasuki discovered a versatile and highly enantioselective route for epoxidation of olefins by Mn(III) complexes [5–8]. Inorganic chemists are trying to synthesize the mononuclear manganese enzymes which have biomimetic importance [9]. In mononuclear enzymes, manganese is believed to shuttle between Mn(II) and Mn(III). Among these enzymes only manganese superoxide dismutase (MnSOD) adopts a trigonal-bipyramidal (tbp) arrangement with an N_3O_2 donor set [10]. Although various coordination geometries are possible and square-pyramidal (sqpy) geometry is common for Mn(III), trigonal-bipyramidal stereochemistry is still rare. Generally five-coordinate trigonal-bipyramidal geometry is stabilized in Mn(II) by unidentate and simple tridentate ligands (like terpyridine) [11–13]. The Mn(III) complex, [Mn(trenMe$_6$)Br]Br (where Me$_6$tren is tris(2-dimethylaminoethyl)amine) is

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also known [12] to be trigonal-bipyramidal. An example of Mn(III) trigonal-bipyramidal complex, *trans*-$MnI_3(PMe_3)_2$, was isolated by Beagley *et al.* [14] by oxidation of MnI_2 in excess of Me_3P. The anion in $(PhCH_2NEt_3)_2[Mn_2(ptt)_2]$ possesses C_i symmetry with the center of inversion crystallographically imposed [15]. This anion can be described as an Mn(III) dimer containing two bridging tetradentate tetrathiolates, $C_6H_{10}S_6^{4-}$, in which Mn geometries are approximately trigonal-bipyramidal. McAuliffe *et al.* [16] report a manganese(III) complex, chlorobis(*N*-phenylsalicylideneaminato-*O*,*N*)manganese(III) with trigonal-bipyramidal structure based on X-ray crystal structure analysis. Rana *et al.* [17] synthesized several five- and six-coordinate manganese(III) complexes involving orthohydroxyacetophenone-picoloyl hydrazone and orthohydroxyacetophenone-isonicotinoyl hydrazone. Depending on pH of the reaction five-coordinate complexes may adopt square-pyramidal or trigonal-bipyramidal geometry. Very recently Sanders *et al.* [18] reported a manganese(III) complex [Mn(III)LI] having trigonal-bipyramidal structure, where L is the dianion of the Schiff base derived from condensation of (±)2,2′-diamino-6,6′-dimethylbiphenyl with 5-tert-butylsalicylaldehyde. Shirin *et al.* [19] reported an Mn(III) trigonal-bipyramidal complex with a tripodal ligand based on tris[*N*-alkylcarbamoylmethyl)amine. Seela *et al.* [20] reported two Mn(III) complexes $(NEt_4)_2[Mn_2(edt)_2]$ (where edt^{2-} is ethane 1,2-dithiolate) and $(NEt_3Bu)_2[Mn_2(pttd)_2]$ (where $pttd^{2-}$ is propen-1,2,3-trithiolate) in which Mn(III) geometries are intermediate between square-pyramidal and trigonal-bipyramidal. Most of the manganese(III) complexes studied for their biological activities and catalytic activities are either square-pyramidal or octahedral. Solid state properties like electrical and optical properties of the manganese(III) complexes with Schiff bases have never been studied.

Density functional theory (DFT) proved to be an effective tool to investigate similar Mn and Fe-based systems, although performances of different functionals are a matter of debate [21–36]. We used the most popular B3LYP (further information can be found in section 3) to obtain the structures of our complexes.

We have been contemplating flexible tetradentate N_2O_2 and N_4 Schiff-base ligands to synthesize Mn(III) complexes having Mn(III) distorted trigonal-bipyramidal and square-pyramidal geometries. We use two of our recently synthesized tetradentate Schiff-base ligands, *N*,*N*′-(2-hydroxy)propylenebis(acetylacetoneimine) (abbreviated to H_2L^1) and *N*,*N*′-(2-hydroxy)propylenebis(2-imino-3-oximino)butane (abbreviated to H_2L^2) to synthesize eight new Mn(III) complexes, [Mn(III)(Lig)(X)] (where Lig stands for the dianion of the Schiff-base ligands and X stands for CH_3COO^-, Cl^-, Br^-, I^-). The backbone of H_2L^1 might provide flexibility to attain the desired Mn(III) geometries in **1**–**4**. As we were unable to grow suitable crystals for X-ray crystal structure analysis, we attempted to solve the structural features of the complexes by DFT calculations. This article records the results of this investigation.

2. Experimental

The chemicals used were of AR grade. Solvents and chemicals were purified and dried before use by standard procedures. Elemental analyses were carried out at the Regional Sophisticated Instrumentation Centre, the Central Drug Research Institute, Lucknow, India. Manganese, halogen, and nitrogen contents were also analyzed in our laboratory by conventional methods. Electronic spectra (DMSO) were recorded on Hitachi 200-20 and Shimadzu UV-2401 PC spectrophotometers and infrared (IR) spectra (KBr/Nujol/Hexachlorobutadiene) on Perkin Elmer 1330 and L120-000A FTIR spectrophotometers. Molar conductances were measured using an Elico conductivity bridge. The magnetic susceptibility was determined by the Gouy method. Molecular weight was determined by Rast's method [37, 38].

2.1. *Preparation of the ligands*

The Schiff bases *N*,*N*′-(2-hydroxy)propylenebis(acetylacetoneimine) (abbreviated to H_2L^1) and *N*,*N*′-(2-hydroxy)propylenebis(2-imino-3-oximino)butane (abbreviated to H_2L^2) were prepared by our previously published methods [5, 39–42] involving condensation of 1,3-diaminopropane-2-ol with acetylacetone and diacetylmonoxime, respectively.

2.2. *Preparation of the manganese(III) complexes*

2.2.1. [Mn(L^1)(Cl)] (1). This brown compound was prepared by the addition of lithium chloride (1.05 g, 25 mmol) to a refluxing (1 h) mixture of manganese(III) acetate, dihydrate (6.7 g, 25 mmol), and H_2L^1 (6.35 g, 25 mmol). The solid compound that separated on slow evaporation was washed with a mixture of benzene-petroleum ether (1 : 1, v/v) and dried in a vacuum desiccator. Yield: 5.14 g (60%); m.p. 290°C(d). Anal. Calcd for $C_{13}H_{20}MnN_2O_3Cl$ (%): C, 45.56; H, 5.88; N, 8.17; Cl, 10.35; Mn, 16.03. Found (%): C, 45.82; H, 5.62; N, 8.0; Cl, 10.78; Mn, 16.5. Λ_M, 13.8 $\Omega^{-1}\,cm^2\,mol^{-1}$, μ_{eff}, 4.79 B.M.

2.2.2. [Mn(L^1)(Br)] (2). This brown compound was prepared by following the method used in the preparation of [Mn(L^2)(Cl)] (**1**), using lithium bromide instead of lithium chloride employing same molar ratios of the reactants. Yield: 6.3 g (65%); m.p. 298°C(d). Anal. Calcd for $C_{13}H_{20}MnN_2O_3Br$ (%): C, 40.33; H, 5.2; N, 7.23; Br, 20.64; Mn, 14.19. Found (%): C, 40.52; H, 5.7; N, 7.02; Br, 20.82; Mn, 14.9. Λ_M, 12.0 $\Omega^{-1}\,cm^2\,mol^{-1}$, μ_{eff}, 4.8 B.M.

2.2.3. [Mn(L^1)(I)] (3). This reddish-brown compound was prepared by following the method used for [Mn(L^1)(Cl)] (**1**), using lithium iodide in place of lithium chloride. Yield: 6.5 g (60%); m.p. 292°C(d). Anal. Calcd for $C_{13}H_{20}MnN_2O_3I$ (%): C, 35.96; H, 4.64; N, 6.45; I, 29.23; Mn, 12.65. Found (%): C, 35.0; H, 4.78; N, 6.98; I, 29.08; Mn, 12.50. Λ_M, 11.8 $\Omega^{-1}cm^2\,mol^{-1}$, μ_{eff}, 4.79 B.M.

2.2.4. [Mn(L^1)(CH_3COO)] (4). Manganese(III) acetate, dihydrate, $Mn(CH_3COO)_3 \cdot 2H_2O$ (1.34 g, 5 mmol) was added to an ethanolic solution (50 mL) of H_2L^1 (1.27 g, 5 mmol) and the mixture was refluxed for about an hour and filtered while hot. The volume of the filtrate was then reduced to half and cooled to ~5°C when dark brown solid separated out, was filtered off, washed with a mixture of benzene-petroleum ether (1 : 1, v/v), and dried in a vacuum desiccator. Yield: 1.09 g (~60%);

m.p. 295°C(d). Anal. Calcd for $C_{15}H_{23}MnN_2O_5$ (%): C, 49.18; H, 6.33; N, 7.64; Mn, 15.0. Found (%): C, 49.3; H, 6.92; N, 7.99; Mn, 15.22. Λ_M, 22.2 $\Omega^{-1}\,cm^2\,mol^{-1}$, μ_{eff}, 4.82 B.M.

2.2.5. [Mn(L^2)(Cl] (5).

This brown compound was prepared by the addition of lithium chloride (1.05 g, 25 mmol) to a refluxing (1 h) mixture of manganese(III) acetate, dehydrate (6.7 g, 25 mmol), and H_2L^2 (6.4 g, 25 mmol). The solid compound that separated on slow evaporation was washed with a mixture of benzene-petroleum ether (1 : 1, v/v) and dried in a vacuum desiccator. Yield: 5.15 g (60%); m.p. 239°C(d). Anal. Calcd for $C_{11}H_{18}MnN_4O_3Cl$ (%): C, 38.32; H, 5.26; N, 16.25; Cl, 10.28; Mn, 15.94. Found (%): C, 38.40; H, 5.33; N, 16.45; Cl, 10.57; Mn, 15.99. Λ_M, 8.9 $\Omega^{-1}cm^2\,mol^{-1}$, μ_{eff}, 4.88 B.M.

2.2.6. [Mn(L^2)(Br)] (6).

This brown compound was prepared by following the method used in the preparation of [Mn(L^1)(Cl)] (**5**), using lithium bromide instead of lithium chloride, employing the same molar ratios of the reactants. Yield: 6.3 g (65%); m.p. 248°C(d). Anal. Calcd for $C_{11}H_{18}MnN_4O_3Br$ (%): C, 33.95; H, 4.66; N, 14.39; Br, 20.54; Mn, 14.12. Found (%): C, 34.0; H, 4.78; N, 14.46; Mn, 14.0. Λ_M, 10.0 $\Omega^{-1}\,cm^2\,mol^{-1}$, μ_{eff}, 4.84 B.M.

2.2.7. [Mn(L^2)(I)] (7).

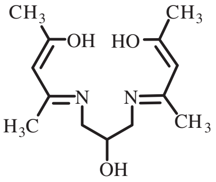
This reddish-brown compound was prepared by following the method used for [Mn(L^1)(Cl)] (**5**), using lithium iodide in place of lithium chloride. Yield: 6.5 g (65%); m.p. 238°C(d). Anal. Calcd for $C_{11}H_{18}MnN_4O_3I$ (%): C, 30.29; H, 4.16; N, 12.84; I, 29.10; Mn, 12.59. Found (%): C, 30.49; H, 4.29; N, 12.58; I, 29.0; Mn, 12.72. Λ_M, 14.8 $\Omega^{-1}\,cm^2\,mol^{-1}$, μ_{eff}, 4.78 B.M.

2.2.8. [Mn(L^2)(CH$_3$COO)] (8).

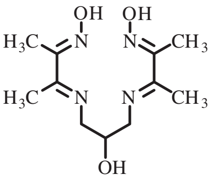
Manganese(III) acetate dihydrate, $Mn(CH_3COO)_3 \cdot 2H_2O$ (1.34 g, 5 mmol) was added to an ethanolic solution (50 mL) of H_2L^2 (1.28 g, 5 mmol) and the mixture was refluxed for an hour and filtered while hot. The volume of the filtrate was then reduced to half and cooled to ~5°C when dark brown solid separated, was filtered off, washed with a mixture of benzene-petroleum ether (1 : 1, V/V), and dried in a vacuum desiccator. Yield: 1.10 g (~60%); m.p. 239°C(d). Anal. Calcd for $C_{13}H_{21}MnN_4O_5$ (%): C, 42.39; H, 5.74; N, 15.21; Mn, 14.92. Found (%): C, 42.60; H, 5.45; N, 15.80; Mn, 14.88. Λ_M, 18.8 $\Omega^{-1}\,cm^2\,mol^{-1}$, μ_{eff}, 4.8 B.M.

3. Results and discussion

Reactions of 1,3-diaminopropane-2-ol with acetylacetone and diacetylmonoxime yielded quadridentate Schiff bases *N*,*N*′-(2-hydroxy)propylenebis(acetylacetoneimine) (abbreviated to H_2L^1) and *N*,*N*′-(2-hydroxy)propylenebis(2-imino-3-oximino)butane (abbreviated to H_2L^2), respectively.



H_2L^1



H_2L^2

The manganese(III) complexes $[Mn(L^1)(CH_3COO)]$ (**4**) and $[Mn(L^2)(CH_3COO)]$ (**8**) were prepared by the reactions of H_2L^1 and H_2L^2 with $[Mn(CH_3COO)_3] \cdot 2H_2O$ in ethanol under nitrogen. The complexes $[Mn(L^1)(X)]$ (where X = Cl (**1**); X = Br (**2**); X = I (**3**)) and $[Mn(L^2)(X)]$ (where X = Cl (**5**); X = Br (**6**); X = I (**7**)) were isolated by addition of appropriate lithium halides to the refluxing (1 h) mixture of manganese(III) acetate dihydrate and H_2L^1 and H_2L^2 (all in equimolar quantities).

3.1. *Computational methods and DFT results*

Since repeated attempts to obtained suitable crystals for structural analyses were not successful, DFT was used to characterize the structures of these complexes. The B3LYP method [43, 44] implemented in Gaussian 03 code [45] with Dunning and Huzinaga valence double-ζ basis functions for first-row elements [46] and effective core-potential functions for halogens and Mn [47] were used in this investigation. The B3LYP/LanL2DZ method has been found successful [26, 27, 48–52] in predicting structures of a wide range of transition metal complexes including Mn complexes. All geometries were fully optimized using analytical gradient technique without imposing any symmetry constraints. Unrestricted B3LYP were used for triplet and quintet states of all complexes considered in this study. Subsequently, harmonic vibrational analyses were carried out for the minima located on the corresponding molecular potential energy hypersurface.

Complexes **1**–**3** and **5**–**8** showed two conformers and the most stable structures are shown in figures 1 and 2; the rest are summarized in figure S1. For **4**, only one conformer was found. It can be seen from table 1 that complexes exhibit both trigonal-bipyramidal and square-pyramidal structures in different states. The $\langle S^2 \rangle$ values indicate quintet and triplet states are nearly pure, and minor spin contamination has been projected out to get pure states. Vibrational analyses showed no imaginary vibrational frequency, indicating a local minimum for all cases.

Relative energies of different conformers in different states, summarized in the left three columns of table 1, indicate that for all cases the high-spin quintet state (^5A) is the most stable structure. The low-spin triplet (^3A) states are 14–24 kcal mol^{-1} less stable than their corresponding quintet states, and the singlet states are least stable for all eight complexes. Based on the large energy difference between triplet and quintet states, high spin ^5A state is the ground state for all complexes, as found in many other Mn(III) complexes [26, 27, 53–56].

The most stable structures of **1**–**3** are trigonal-bipyramidal (**1A**, **2A**, and **3A** in figure 1) in their high-spin ^5A state, and those structures are 11.0 kcal mol^{-1} more stable than their square-pyramidal or tbp structures (**1B**, **2B**, and **3B** in figure S1); this

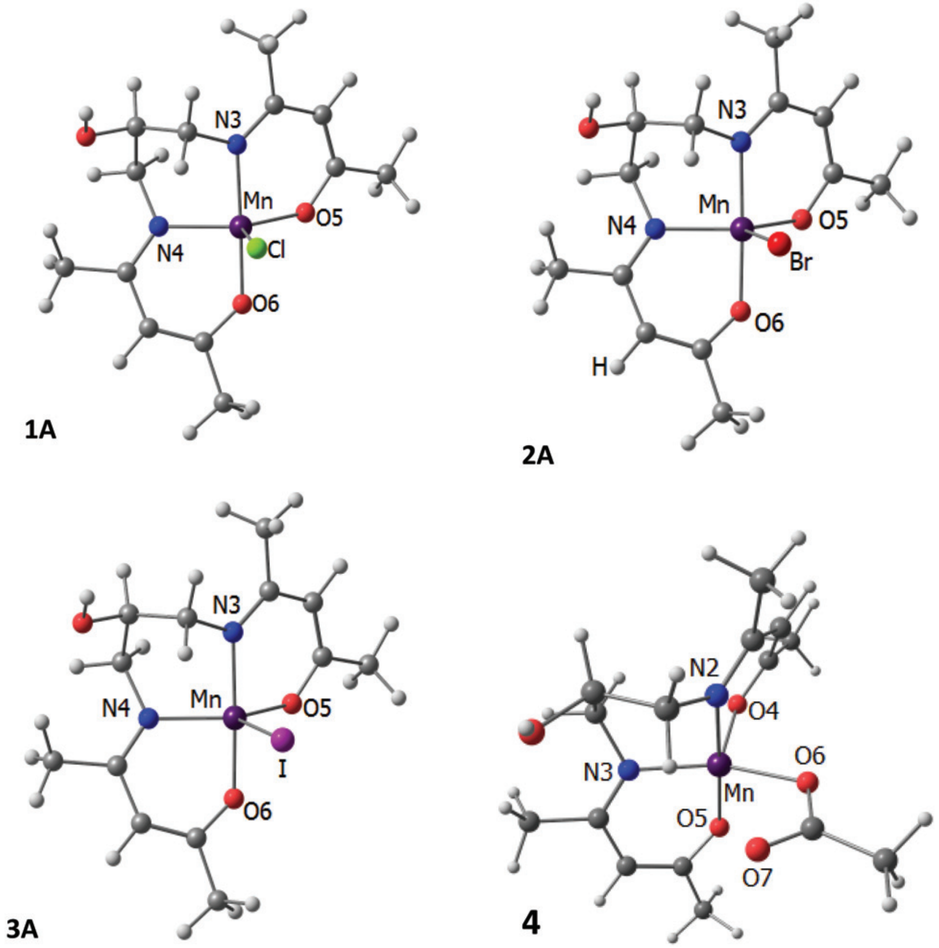


Figure 1. DFT optimized structures of [MnL^1]Cl (**1A**), [MnL^1]Br (**2A**), [MnL^1]I (**3A**), and [MnL^1]CH_3COO (**4**) in their high-spin ^5A state. Important geometric parameters are summarized in table 2.

difference is almost the same for X = Cl, Br, and I in ^5A state. Important geometric parameters of the quintet state of **1A–4** are summarized in table 2. In **1A–3A**, the halide (Cl/Br/I) occupies the equatorial position with N4 and O5. The N3–Mn–O6 axial angle is 175° in **1A** and reduces as Cl is replaced by Br to I. The axial angle (N2–Mn–O5) in **4** deviates by 8° and may be due to steric effect of CH_3COO. We also explored the possibility of an octahedral structure of **4** where acetate is bidentate. However, geometry optimization of such structure returned to the distorted tbp structure as shown in figure 1, where the Mn–O7 distance is 2.639 Å. The spin density on Mn in **1A–4** is about 3.8e. Therefore, we conclude that [Mn(L^1)(X] (where X = Cl, Br, I, and CH_3COO) is Mn(III).

The complexation of *N*,*N*′-(2-hydroxy)propylenebis(2-imino-3-oximino)butane (H_2L^2) with Mn(III) acetate results in square-pyramidal structure for **5A–7A** and tbp for **8A** (shown in figure 2) in their high-spin quintet state. The presence of O6–H···X (X–Cl, Br, and I) hydrogen bond in the halogenated complexes (**5A–7A**) enhanced

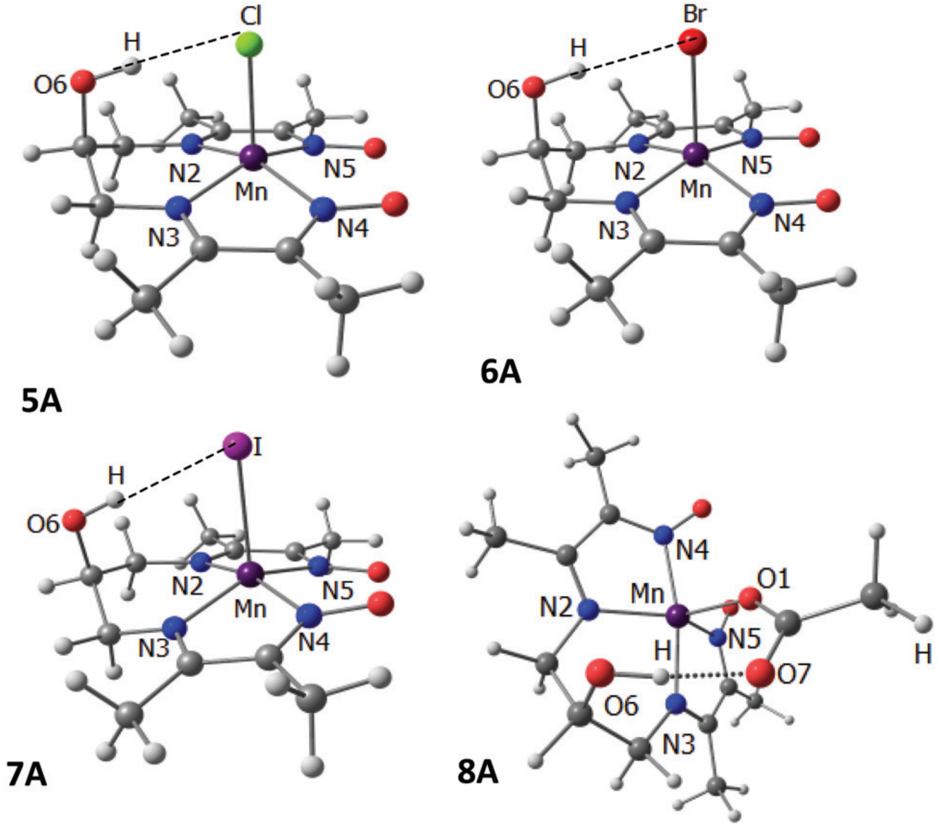


Figure 2. DFT optimized structures of $[MnL^2]Cl$ (**5A**), $[MnL^2]Br$ (**6A**), $[MnL^2]I$ (**7A**), and $[MnL^2]CH_3COO$ (**8A**) in their ^5A state. O_6–H $\cdots$ X (X = Cl, Br, and I) H-bond is shown by dotted line. Important geometric parameters are summarized in table 2.

stability compared to their corresponding non-hydrogen bonded counterparts (**5B**–**7B** in figure S1). As expected, hydrogen-bond energy decreases in the series and the order is: **5A** (3.6 kcal mol^{-1}) > **6A** (2.5 kcal mol^{-1}) > **7A** (1.6 kcal mol^{-1}). The other signature of weakening H-bond strength in the series is reflected in lengthening of the X $\cdots$ H bond distance from 2.22 Å in **5A** to 2.40 Å in **6A** to 2.61 Å in **7A**. The strongest H-bond of the series is found in **8A**, where the O $\cdots$ H distance is shortest. The optimization failed to locate the triplet state of **8 A** due to high-spin contamination. The spin density on Mn is about 4.0 e, confirming $[Mn(L^2)(X)]$ are Mn(III) species.

3.2. *Molar conductance and magnetic moments*

Molar conductance values of the isolated manganese(III) complexes in DMSO and DMF are 8.9–22.8 Ω^{-1} cm^2 mol^{-1} for 10^{-3} mol L^{-1} solution, suggesting non-electrolytic nature (immediate after dissolution) [57]; after 4–5 h the molar conductance values of **4** and **8** are increased to 42.5 and 46.2 Ω^{-1} cm^2 mol^{-1}, respectively, suggesting 1 : 1 electrolytes due to the replacement of CH_3COO^- by DMSO (see spectral discussion).

Table 1. Relative energies (in kcal mol^{-1}) of some complexes.

	Relative energies of different states			Relative energies (E(B)–E(A)) of different conformers in different states[d]		
Complexes	Quintet[a]	Triplet[a]	Singlet[c]	Quintet	Triplet	Singlet
1A	0.0 tbp	24.3 tbp	44.2	0.0	0.0	0.0
1B	0.0 sqpy	19.1 sqpy	45.9	10.9	5.7	12.6
2A	0.0 tbp	25.9 tbp	44.8	0.0	0.0	0.0
2B	0.0 sqpy	19.5 sqpy	45.6	11.1	4.7	11.9
3A	0.0 tbp	27.3 tbp	45.4	0.0	0.0	0.0
3B	0.0 tbp	20.1 sqpy	45.6	11.0	3.8	11.2
4	0.0 tbp	14.1 tbp	41.3			
5A	0.0 sqpy	20.4 sqpy	46.0	0.0	0.0	0.0
5B	0.0 sqpy	19.7 sqpy	45.5	3.6	2.9	3.0
6A	0.0 sqpy	21.1 sqpy	46.4	0.0	0.0	0.0
6B	0.0 sqpy	20.6 sqpy	45.5	2.5	2.0	1.6
7A	0.0 sqpy	22.0 sqpy	46.3	0.0	0.0	0.0
7B	0.0 sqpy	21.7 sqpy	45.7	1.6	1.2	0.9
8A	0.0 tbp	NC[b]	40.6	0.0		0.0
8B	0.0 sqpy	23.7 sqpy	39.7	5.2		4.4

All structures along with DFT energy and spin density of Mn are summarized in figure S1.

[a] tbp and sqpy stand for trigonal-bipyramidal and square-pyramidal, respectively.

[b] NC stands for not converged to an optimized structure.

[c] All singlet states are tbp.

[d] Energies relative to most stable conformers **A**.

Complexes **1**–**8** are all soluble in DMSO, DMF, pyridine, ethanol, chloroform, and benzene and all are paramagnetic with room temperature magnetic moments in the range 4.79–4.88 B.M., normal for high-spin ($S=2$) discrete mononuclear manganese(III) complexes [39]. These values show the absence of exchange or super exchange interactions. The complexes do not show any epr signals. Even-spin ($S=2$) manganese(III) monomers are epr-silent particularly at $g\sim 2$ region, because of a combination of non-Kramers degeneracy, zero-field splitting and adverse relaxation rate effect [58]. This observation also supports the presence of manganese(III) in these complexes [59].

3.3. *Vibrational spectroscopy*

IR spectra of the ligands (table 3) show medium to strong bands at 3132–3340 cm^{-1} assignable to ν(OH) {=C(CH$_3$)OH} for H_2L^1 and a band at 3000–3400 cm^{-1} assignable to ν(OH) (oxime) for H_2L^2. The presence of secondary OH in these ligands has been demonstrated by the appearance of a band around 3400 cm^{-1}. The broad nature of the bands suggests hydrogen-bonding [60–62]. The ν(C=N) (azomethine) in H2L1 and H_2L^2 are at 1610–1620 cm^{-1} as very strong bands. The ν(C=N) (oxime linkage) in H_2L^2 is possibly obscured by the other strong band at 1615 cm^{-1}. The ν(N–O) for H_2L^2 is observed as a strong band [63] at 940 cm^{-1}. The ν(C–O) (secondary alcohol) at 1350 cm^{-1} in H_2L^1 and H_2L^2 remains unchanged in the metal complexes, demonstrating non-involvement of this group in these complexes [63]. Disappearance of bands at 3000–3300 cm^{-1} suggests deprotonation of OH {=C(CH$_3$)OH of H_2L^1} and oxime OH (of H_2L^2) allowing these ligands to function as dibasic quadridentate. However, a broad

Table 2. Geometric parameters (length in Å and angles in degree) of the most stable conformer in quintet state of **1**–**8**.[a]

1A (3.8)					
Mn–Cl	2.312	N3–Mn–O6	174.8	N3–Mn–Cl	91.2
Mn–N3	1.992	Cl–Mn–N4	103.4	N3–Mn–N4	91.6
Mn–N4	1.916	Cl–Mn–O5	153.1	N3–Mn–O5	89.5
Mn–O5	1.892	N4–Mn–O5	103.5	O6–Mn–Cl	88.6
Mn–O6	1.920	O6–Mn–N4	93.5	O6–Mn–O5	88.3
2A (3.8)					
Mn–Br	2.597	N3–Mn–O6	177.5	N3–Mn–Br	90.6
Mn–N3	1.987	Br–Mn–N4	112.7	N3–Mn–N4	89.5
Mn–N4	2.036	Br–Mn–O5	114.4	N3–Mn–O5	89.3
Mn–O5	1.954	N4–Mn–O5	132.9	O6–Mn–Br	91.7
Mn–O6	1.879	O6–Mn–N4	88.7	O6–Mn–O5	90.7
3A (3.8)					
Mn–I	2.816	N3–Mn–O6	178.1	N3–Mn–I	90.4
Mn–N3	1.986	I–Mn–N4	114.8	N3–Mn–N4	89.5
Mn–N4	2.034	I–Mn–O5	112.6	N3–Mn–O5	89.6
Mn–O5	1.953	N4–Mn–O5	132.5	O6–Mn–I	90.8
Mn–O6	1.878	O6–Mn–N4	88.7	O6–Mn–O5	91.4
4 (3.9)					
Mn–N2	1.986	N2–Mn–O5	172.1	N2–Mn–N3	88.7
Mn–N3	2.026	N3–Mn–O4	107.2	N2–Mn–O4	87.8
Mn–O4	2.055	N3–Mn–O6	157.8	N2–Mn–O6	89.9
Mn–O5	1.898	O4–Mn–O6	94.8	O5–Mn–N3	89.3
Mn–O6	1.997	O5–Mn–O4	100.2	O5–Mn–O6	89.1
5A (4.1)					
Mn–Cl	2.403	N2–Mn–N4	159.9	Cl–Mn–N2	98.9
Mn–N2	2.030	N3–Mn–N5	156.6	Cl–Mn–N3	100.4
Mn–N3	2.033	N2–Mn–N3	92.9	Cl–Mn–N4	100.8
Mn–N4	2.057	N2–Mn–N5	79.8	Cl–Mn–N5	102.6
Mn–N5	2.062	N3–Mn–N4	79.9	N4–Mn–N5	99.5
H···Cl	2.223				
6A (4.1)					
Mn–Br	2.568	N2–Mn–N4	157.4	Br–Mn–N2	101.1
Mn–N2	2.029	N3–Mn–N5	159.5	Br–Mn–N3	100.4
Mn–N3	2.028	N2–Mn–N3	93.0	Br–Mn–N4	101.3
Mn–N4	2.060	N2–Mn–N5	79.9	Br–Mn–N5	99.8
Mn–N5	2.057	N3–Mn–N4	79.9	N4–Mn–N5	99.4
H···Br	2.400				
7A (4.0)					
Mn–I	2.770	N2–Mn–N4	165.6	I–Mn–N2	97.6
Mn–N2	2.013	N3–Mn–N5	150.9	I–Mn–N3	105.0
Mn–N3	2.023	N2–Mn–N3	92.9	I–Mn–N4	96.4
Mn–N4	2.043	N2–Mn–N5	80.1	I–Mn–N5	103.9
Mn–N5	2.061	N3–Mn–N4	80.0	N4–Mn–N5	100.0
H···I	2.609				
8A (4.0)					
Mn–O1	1.966	N3–Mn–N4	166.8	N4–Mn–O1	95.5
Mn–N2	2.029	N2–Mn–O1	124.2	N4–Mn–N5	100.0
Mn–N3	2.005	N2–Mn–N5	135.0	N3–Mn–O1	97.5
Mn–N4	2.029	O1–Mn–N5	100.7	N3–Mn–N5	79.5
Mn–N5	2.094	N4–Mn–N2	79.8	N3–Mn–N2	91.2
H···O7	1.612				

[a] Values in parentheses are spin density on Mn.

band at 3400 cm^{-1} (secondary alcohol) complicates this interpretation. Bands due to C=N (both azomethine and oxime) shift to lower frequencies by 10–25 cm^{-1} compared to free ligand values, indicating bonding through N_2O_2 ($H_2\mathrm{L}^1$) and N_4 ($H_2\mathrm{L}^2$). IR spectra of **8** show ν_{asym}COO and ν_{sym}COO at 1545 cm^{-1} and 1425 cm^{-1}, respectively;

Table 3. Selected experimental IR frequencies (cm^{-1}) with tentative assignments. The second values are from DFT unscaled frequencies for most stable conformers of **1**–**8**.

	Complex							
Bands	**1A**	**2A**	**3A**	**4**	**5A**	**6A**	**7A**	**8A**
νMn–N	390	360	390	388	380	383	384	365
					359	358	361	351
νMn–O	526	492	485	500	–	–	–	504
								513
νMn–X	283	282	220	–	290	255	219	–
	286	262	256		308	269	192	
νC=N	1593	1568	1601	1586	1580	1589	1573	1583
	1607	1605	1605	1599	1557	1554	1550	1574
νOH	3230	3253	3340	3229	3347	3132	3156	3169
	3680	3680	3681	3681	3443	3459	3476	3065
νCO(alcohol)	1348	1340	1319	1310	1319	1340	1365	1356
νC–H str.	3016	3060	3115	3063	3187	2967	3025	3015
νC–H str.	3076	3105	3187	3132	3238	3017	3073	3109
νC–H bend.	1105	1132	1138	1101	1142	1159	1168	1169
νC–H bend.	1237	1252	1274	1269	1251	1270	1251	1282
νC–H bend.	1399	1413	1430	1372	1399	1362	1385	1388
νN–O	–	–	–	–	989	957	970	993
					1178	1179	1175	1171

the difference between these two bands is 120 cm^{-1}, indicating unidentate acetate [64–66]. Similarly the monodentate nature of acetate group in **4** could be inferred from IR spectral data.

Most vibrational modes are mixed and present DFT calculation could not identify any pure mode for complexes. Some theoretical frequencies ($\nu_{\text{Mn–X}}$, ν_{CN}, ν_{OH}, and ν_{NO}) are summarized in table 3. These bands (except the O–H band) are not pure at all but have identifiable contributions. The large differences between theoretical and experimental results may be due to the amorphous nature of the sample and possible H-bonding with solvents and conjugation with different modes. For example, theoretical values of O–H stretching modes of **1**–**8** are significantly larger than their corresponding experimental values. This difference may be due to solvent effect or interaction between species *via* inter-molecular H-bonding which have not been considered in the theoretical calculations. It is well-known [66] that the O–H stretching mode shifts to lower frequency [67] when participating in conventional H-bonding. Theoretical $\nu_{\text{Mn–X}}$ and ν_{CN} values are close to the corresponding experimental values.

3.4. *Electronic spectra*

Nujol mull electronic absorption spectra of **1**–**4** and **8** show bands at 16,000–16,800 cm^{-1}, 20,000–21,000 cm^{-1}, 25,500–26,000 cm^{-1}, and 34,500–36,000 cm^{-1}. Two d–d transitions are observed, while the high energy bands may be due to charge transfer. The spectra are consistent with five-coordinate geometry around manganese(III) [68], although a choice of square-pyramidal and trigonal-bipyramidal structure is difficult, because the energy difference between two structures is small [68]. The flexible –CH$_2$–CH(OH)–CH$_2$– backbone of the Schiff bases might help the ligand

Table 4. Observed ligand field bands.

Complex	Band maxima (cm^{-1})
$[Mn(L^1)(CH_3COO)]$ (**4**)	20,000
$[Mn(L^1)(Cl)]$ (**1**)	18,500
$[Mn(L^2)(CH_3COO)]$ (**8**)	20,100
$[Mn(L^2)(Cl)]$ (**5**)	18,000

attain a *cis*-β structure in the complexes and monodentate ligand may take one axial position to complete the trigonal-bipyramidal structure/geometry. The energy level diagram for trigonal-bipyramidal complex of a d^4 ion is not available and no attempts have been made to assign the electronic spectral bands. However, similar band positions were used to correlate with the five-coordinate trigonal-bipyramidal structure for manganese(III) complexes [17, 19].

The electronic absorption spectra of **5**–**7** in methanol consist of an intense band at 23,800 cm^{-1} ($\log \varepsilon = 3.3$) and a broad band at 19,700 cm^{-1} ($\log \varepsilon = 2.9$); bands at higher wavenumbers could arise as a result of charge transfer [4, 5], whereas the absorption band at 19,700 cm^{-1} can be assigned to the ${}^5E_g \rightarrow {}^5T_{2g}$ transition (in O_h) [69]. The broadness of the band in the visible region with increased intensity is most likely due to lowering of symmetry from octahedral.

Five-coordinate complexes can be easily six-coordinate, pseudo-octahedral by forming adducts with electron-donating groups from solvent or the framework. A broad ligand field band at 20,400 cm^{-1} is diagnostic for C_{4V} symmetry [70]. From the elemental analysis and other properties it seems that **5**–**7** are five-coordinate with square-pyramidal configuration (C_{4v}) with the anion occupying the axial position [71–73]. The square planar arrangement of the Schiff base having N_4 donors occupies the four equatorial positions [64–66].

In acetate complexes the solution species on prolonged standing will be $[Mn(L^1)(DMSO)_2]^+$ or $[Mn(L^2)(DMSO)_2]^+$ due to dissociation of acetate. The molar conductance of the solution supports this dissociation (see above). Due to lower ligand field strength of DMSO, the d_z^2 orbital will be less destabilized. As a result, the ligand field transition will be blue shifted in acetate complexes compared to chloride complexes. As table 4 shows, this is indeed the case. For manganese(III) Schiff-base complexes with the C_{4v} micro-symmetry, similar situations have been observed [73, 74].

4. Conclusion

We have characterized eight new manganese(III) complexes [Mn(III)(Lig)(X)] (where Lig stands for the dianion of the Schiff bases and $X = Cl^-$, Br^-, I^-, CH_3COO^-) by physio-chemical methods. The spectroscopic data of metal complexes indicate that the metal ions are coordinated through N_2O_2 (H_2L^1) and N_4 (H_2L^2). The magnetic moments of the complexes show no interaction between metal centers. The DFT calculation showed trigonal-bipyramidal for H_2L^1 and square-pyramidal geometries for H_2L^2 complexes in quintet ground states. Theoretical IR bands of some key bonds are close to the corresponding experimental IR spectra supporting trigonal-bipyramidal and square-pyramidal structures. H_2L^1 is more flexible than H_2L^2 facilitating formation of trigonal-bipyramidal Mn(III) geometries in the complexes.

Supplementary material

S1: DFT optimized structures of singlet (s), triplet (t), and quintet (q) states of all complexes. tbp and sqpy stand for trigonal-bipyramidal and square-pyramidal, respectively. DFT energies (E) and spin density of Mn are also given.

S2: DFT optimized cartesian coordinates of all complexes in different states. These data can be obtained free of charge.

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References

[1] C.F. Yocum, V.L. Pecoraro. *Curr. Opin. Chem. Biol.*, **3**, 182 (1999).
[2] T.M. Rajendiran, M.T. Caudle, M.L. Kirk, I. Setyawati, J.W. Kampf, V.L. Pecoraro. *J. Biol. Inorg. Chem.*, **8**, 283 (2003).
[3] M.U. Triller, W.-Y. Hseih, V.L. Pecoraro, A. Rompel, B. Krebs. *Inorg. Chem.*, **41**, 5554 (2002).
[4] M. Alexiou, C. Dendrinou-Sharma, A. Karagianni, C. Zaleski, D. Yoder, J.W. Kampf, J.E. Penner-Hahn, V.L. Pecoraro, D.P. Kessissoglou. *Inorg. Chem.*, **42**, 2185 (2003).
[5] K. Dey, S. Biswas, S. Sarkar. *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 1615 (2004).
[6] K. Srinivasan, P. Michaud, J.K. Kochi. *J. Am. Chem. Soc.*, **108**, 2309 (1986).
[7] P.J. Phosphisil, D.H. Carsten, E.N. Jacobsen. *Chem. Eur. J.*, **2**, 974 (1996).
[8] T. Katasuki. *Coord. Chem. Rev.*, **140**, 189 (1995).
[9] N.A. Law, M.T. Caudle, V.L. Pecoraro. *Adv. Inorg. Chem.*, **46**, 305 (1999), and references cited therein.
[10] G.E. Borystahl, H.E. Parge, M.J. Hickey, W.F. Beyer Jr, R.A. Hallewell, J.A. Trainer. *Cell*, **71**, 107 (1992).
[11] L.S. Erre, G. Micera, E. Garribba, A. Cs. Bényei. *New J. Chem.*, **24**, 725 (2000).
[12] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann. *Advanced Inorganic Chemistry*, 6th Edn, p. 757, Wiley, New York (1999).
[13] S.T. Warzeska, F. Micciche, M.C. Mimmi, E. Bouwman, H. Kooijiman, A.L. Spek, R. Reedijk. *J. Chem. Soc., Dalton Trans.*, 3507 (2001).
[14] B. Beagley, C.A. McAuliffe, K. Miuteu, R.G. Pritchard. *J. Chem. Soc., Chem. Commun.*, 658 (1984).
[15] J.L. Seela, K. Folting, R.J. Wang, J.C. Huffman, G. Christou, H.R. Chang, D.N. Hendrickson. *Inorg. Chem.*, **24**, 4454 (1985).
[16] C.A. McAuliffe, R.G. Pritchard, L. Luaces, J.A. Garcia-Vazquez, J. Romero, M.R. Bermejo, A. Sousa. *Acta Cryst.*, **C49**, 587 (1993).
[17] V.B. Rana, J.N. Gurtu, M.P. Teotia. *J. Inorg. Nucl. Chem.*, **42**, 331 (1980).
[18] C.J. Sanders, P.N. O'Shanghnessy, P. Scott. *Polyhedron*, **22**, 1617 (2003).
[19] Z. Shirin, V.G. Yonng, A.S. Borovick. *J. Chem. Soc., Chem. Commun.*, 1967 (1997).

[20] J.L. Seela, M.J. Knapp, K.S. Kolack, H.-R. Chang, J.C. Huffman, D.N. Hendrickson, G. Christou. *Inorg. Chem.*, **37**, 516 (1998).
[21] O. Salomon, M. Reiher, B.A. Hess. *J. Chem. Phys.*, **117**, 4729 (2002).
[22] M. Reiher, O. Salomon, B.A. Hess. *Theor. Chem. Acc.*, **107**, 48 (2001).
[23] T. Lovell, W.-G. Han, T. Liu, L. Noodleman. *J. Am. Chem. Soc.*, **124**, 5890 (2002).
[24] T. Lovell, T. Liu, D.A. Case, L. Noodleman. *J. Am. Chem. Soc.*, **125**, 8377 (2003).
[25] W.-G. Han, T. Lovell, T. Liu, L. Noodleman. *Inorg. Chem.*, **42**, 2751 (2003).
[26] D. Quinonero, D.G. Musaev, K. Morokuma. *Inorg. Chem.*, **42**, 8449 (2003).
[27] I.V. Khavrutskii, R.R. Rahim, D.G. Musaev, K. Morokuma. *J. Phys. Chem. B*, **108**, 3845 (2004); I.V. Khavrutskii, D.G. Musaev, K. Morokuma. *J. Am. Chem. Soc.*, **125**, 13879 (2003).
[28] C.A. Linde, B. Kermark, P.-O. Norrby, M. Svensson. *J. Am. Chem. Soc.*, **121**, 5083 (1999).
[29] T. Strassner, K.N. Houk. *Org. Lett.*, **1**, 419 (1999).
[30] A. Ghosh, E. Gonzalez, T. Vangberg, P.J. Taylor. *Porphyrins Phthalocyanines*, **5**, 345 (2001).
[31] D. Kumar, S.P. De Visser, S. Shaik. *J. Am. Chem. Soc.*, **126**, 5072 (2004).
[32] S.P. De Visser, D. Kumar, S. Cohen, R. Shacham, S. Shaik. *J. Am. Chem. Soc.*, **126**, 8362 (2004).
[33] Y.G. Abashkin, S.K. Burt. *J. Phys. Chem. B*, **108**, 2708 (2004).
[34] Y.G. Abashkin, J.R. Collins, S.K. Burt. *Inorg. Chem.*, **40**, 4040 (2001).
[35] L. Cavallo, H. Jacobsen. *Inorg. Chem.*, **43**, 2175 (2004).
[36] L. Cavallo, H. Jacobsen. *Angew. Chem., Int. Ed.*, **39**, 589 (2000).
[37] K. Rast. *Ber. Dtsch. Chem. Ges.*, **55**, 3727 (1922).
[38] A. Alexander Findlay, J.A. Kitchener. *Practical Physical Chemistry*, 8th Edn, p. 115, Longman, Green & Co., London, New York, Toronto (1954).
[39] K. Dey. *Z. Anorg. Allg. Chem.*, **376**, 209 (1970).
[40] K. Dey. *J. Indian Chem. Soc.*, **48**, 641 (1971).
[41] K. Dey, S.C. Sadhu, N.B. Choudhury, K.K. Chaterjee. *J. Indian Chem. Soc.*, **48**, 973 (1971).
[42] K. Dey, S. Biswas. *J. Indian Chem. Soc.*, **79**, 222 (2002), and references cited therein.
[43] P.J. Steven, F.J. Devlin, C.F. Chablowski, M.J. Frisch. *J. Phys. Chem.*, **98**, 11623 (1994); A.D. Becke. *J. Chem. Phys.*, **98**, 5648 (1993).
[44] C. Lee, W. Yang, R.G. Parr. *Phys. Rev. B*, **37**, 785 (1988).
[45] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople. *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford, CT (2004).
[46] T.H. Dunning Jr, P.J. Hay. In *Modern Theoretical Chemistry*, H.F. Schaefer III (Ed.), Vol. 3, pp. 1–28, Plenum, New York (1976).
[47] P.J. Hay, W.R. Wadt. *J. Chem. Phys.*, **82**, 270 (1985); W.R. Wadt, P.J. Hay. *J. Chem. Phys.*, **82**, 284 (1985).
[48] A.J. Johansson, M.R.A. Blomberg, P.E.M. Siegbahn. *Inorg. Chem.*, **45**, 1491 (2006).
[49] J. Wiebke, A. Moritz, M. Glorius, H. Moll, G. Bernhard, M. Dolg. *Inorg. Chem.*, **47**, 3150 (2008).
[50] J. Gracia Budrìa, S. Raugei, L. Cavallo. *Inorg. Chem.*, **45**, 1733 (2006).
[51] P.L.W. Tregenna-Piggott. *Inorg. Chem.*, **47**, 448 (2008).
[52] Q. Scheifele, C. Riplinger, F. Neese, H. Weihe, A.-L. Barra, F. Juranyi, A. Podlesnyak, P.L.W. Tregenna-Piggott. *Inorg. Chem.*, **47**, 439 (2008).
[53] J. Conradie, E. Tangen, A. Ghosh. *J. Inorg. Biochem.*, **100**, 707 (2006).
[54] L. Cavallo, H. Jacobsen. *J. Org. Chem.*, **68**, 6202 (2003).
[55] H. Hirao, K.-B. Cho, S. Shaik. *J. Biol. Inorg. Chem.*, **13**, 521 (2008).
[56] Y. Yoshioka, H. Sano, M. Mitani. *Bull. Chem. Soc. Japan*, **79**, 1201 (2006).
[57] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[58] L.J. Boucher. *Coord. Chem. Rev.*, **7**, 289 (1972).
[59] J. Limburg, J.S. Vrettos, R.H. Crabtree, G.W. Brudvig, J.C. DePaula, A. Hassan, A.-L. Barra, C. Duboc-Toia, M.-N. Collomb. *Inorg. Chem.*, **40**, 1698 (2001), and references cited therein.
[60] K. Nakamoto. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Edn, pp. 155, 194, Wiley Interscience, New York (1963).
[61] M. Nonayama, S. Tomita, K. Yamasaki. *Inorg. Chim. Acta*, **12**, 33 (1975).
[62] D.K. Rastogi, S.K. Dua, S.K. Sahni. *J. Inorg. Nucl. Chem.*, **42**, 323 (1980).
[63] M.M. Mostafa, K.M. Ibrahim, M.N.H. Moussa. *Transition Met. Chem.*, **9**, 243 (1984).

[64] K. Dey, K.C. Ray. *J. Indian Chem. Soc.*, **50**, 66 (1973); *J. Indian Chem. Soc.*, **50**, 631 (1973).
[65] K. Dey, K.C. Ray, R.L. De. *Indian J. Chem.*, **10A**, 864 (1972).
[66] K. Dey, K.C. Ray. *J. Inorg. Nucl. Chem.*, **37**, 695 (1975), and references cited therein.
[67] Y. Gu, T. Kar, S. Scheiner. *J. Am. Chem. Soc.*, **121**, 9411 (1999).
[68] E.L. Muettertis, R.A. Schunn. *Q. Rev.*, **20**, 245 (1966).
[69] R. Dingle. *Acta Chem. Scand.*, **20**, 33 (1966).
[70] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam (1968).
[71] A. van den Bergen, K.S. Murray, M.J. O'Connor, B.O. West. *Aust. J. Chem.*, **22**, 39 (1966).
[72] L.J. Boucher, V.W. Day. *Inorg. Chem.*, **16**, 1360 (1977).
[73] J.A. Bonadies, M.J. Maroney, V.L. Pecoraro. *Inorg. Chem.*, **28**, 2044 (1989).
[74] R. Shukla, P.K. Bharadwaj. *Indian J. Chem.*, **32A**, 767 (1993).